

Final Report

Title: Mathematical modeling and optimization studies on development of fuel cells for multifarious applications.

AFOSR/AOARD Reference Number: FA2386-08-1-4114

AFOSR/AOARD Program Manager: Dr. Rengasamy Ponappan

Period of Performance: 13 August 2008 – 12 February 2010

Submission Date: 12 May 2010

Principal Investigator:

Professor Ashok Kumar Shukla

Solid-state and Structural Chemistry Unit

Indian Institute of Science, Bangalore 560012, INDIA

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 21 JUN 2010		2. REPORT TYPE Final		3. DATES COVERED 13-08-2008 to 12-02-2010	
4. TITLE AND SUBTITLE Mathematical modeling and optimization studies on development of fuel cells				5a. CONTRACT NUMBER FA23860814114	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Ashok Kumar Shukla				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Indian Institute of Science, Science Institute PO, Bangalore, India, ID, 560012				8. PERFORMING ORGANIZATION REPORT NUMBER N/A	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Asian Office of Aerospace Research & Development, (AOARD), Unit 45002, APO, AP, 96338-5002				10. SPONSOR/MONITOR'S ACRONYM(S) AOARD	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AOARD-084114	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Direct borohydride fuel cells (DBFCs) are among the most energy dense power sources projected for futuristic portable applications. In this project, authors developed a three-dimensional, multicomponent steady-state model for liquid-feed solid polymer electrolyte DBFCs. These fuel cells use sodium borohydride (NaBH₄) in alkaline media as fuel and acidified hydrogen peroxide (H₂O₂) as oxidant. The model employs implementation of phenomenological transport equations for the catalyst layers, diffusion layers and the polymer electrolyte membrane for a liquid feed DBFC. Diffusion of reactants within and between the pores is accounted under the framework of macrohomogeneous porous electrode theory. The kinetic treatment considered for porous structures of the catalyst layers is of Butler-Volmer type. Numerical solutions are achieved after coupling electrochemical reaction kinetics and transport mechanisms in the conservation laws, which explicitly include the effect of concentration and pressure gradients on cell polarization within the bulk catalyst layers. To understand fully the role of model parameters in simulating the performance of the DBFC, its parametric study is also carried out. A study has also been carried out for the experimental validation of the model.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 18	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Abstract

Direct borohydride fuel cells (DBFCs) are among the most energy dense power sources projected for futuristic portable applications. In this project we developed a three-dimensional, multicomponent steady-state model for liquid-feed solid polymer electrolyte DBFCs. These fuel cells use sodium borohydride (NaBH_4) in alkaline media as fuel and acidified hydrogen peroxide (H_2O_2) as oxidant. The model employs implementation of phenomenological transport equations for the catalyst layers, diffusion layers and the polymer electrolyte membrane for a liquid feed DBFC. Diffusion of reactants within and between the pores is accounted under the framework of macrohomogeneous porous electrode theory. The kinetic treatment considered for porous structures of the catalyst layers is of Butler-Volmer type. Numerical solutions are achieved after coupling electrochemical reaction kinetics and transport mechanisms in the conservation laws, which explicitly include the effect of concentration and pressure gradients on cell polarization within the bulk catalyst layers. To understand fully the role of model parameters in simulating the performance of the DBFC, its parametric study is also carried out. A study has also been carried out for the experimental validation of the model.

Objectives

Ideally a single DBFC could produce about 3 V which is close to the voltages achieved with lithium cells and a specific energy of about 17 kWh/kg. However in experimental studies we found them to deliver significantly lower voltage and power. DBFCs require novel electrode designs for optimal catalyst placement, fuel/oxidant management and operational characteristics. These design goals can only be approached by combining experiments with a reliable mathematical modeling of the DBFC systems. This project is in continuation to our earlier project on DBFCs wherein we have successfully developed and demonstrated a 40 W DBFC stack. The objective is to develop a novel mathematical model for solid polymer electrolyte direct borohydride fuel cells. The losses due to overpotential or polarization will be quantified and minimized to achieve higher specific energies of such a fuel cell. Accordingly, a DBFC with a high output voltage would provide a pragmatic gateway to solve the most challenging problem associated with the currently available batteries, namely, their limited energy density.

Introduction

Use of novel chemistries to generate energy efficiently from material abundantly available is in vogue. Alkaline liquid feed Sodium Borohydride (NaBH_4) as fuel and acidified liquid-feed hydrogen peroxide (H_2O_2) as oxidant in a direct borohydride fuel cell (DBFC) has demonstrated much promise in our experiments [1], with more than 30% higher voltage output, compared to H_2/O_2 fuel cells, under similar operating conditions, even though hydrogen constitutes about 11% in sodium borohydride.

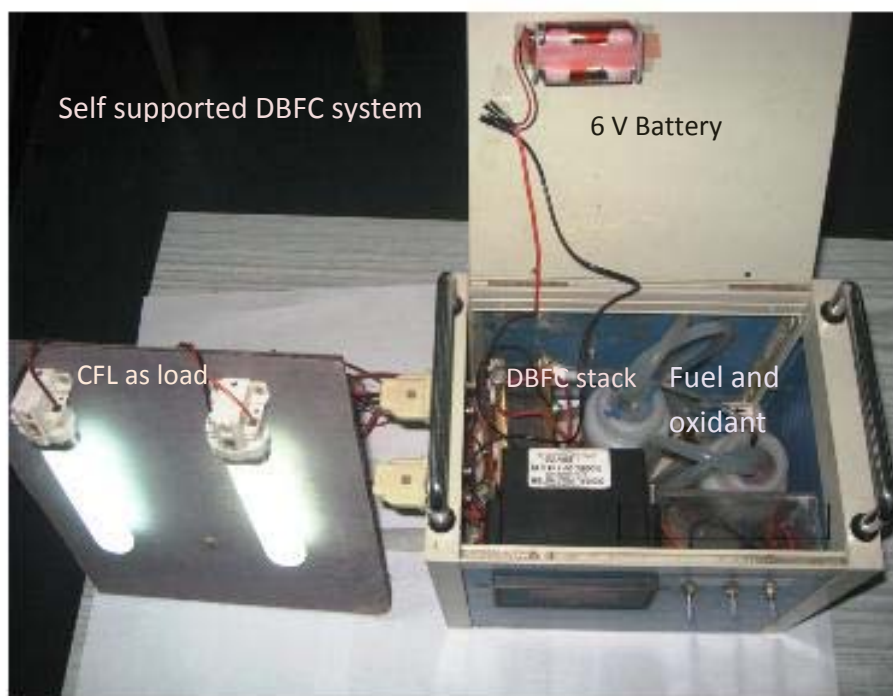


Figure 1. DBFC system demonstrated at US-India workshop on power and energy

Hydrogen peroxide is among the most powerful oxidant used for long in space propulsion [2]. Recently its use in fuel cells is found to be ideally suitable: *Powerful* using appropriate electrocatalysts H_2O_2 is converted into hydroxyl (OH^-) ions, which has reactivity second only to fluoride ions (F^-). *Economical* current production at over a billion pounds a year results in its low cost. *Environmental friendly* H_2O_2 exists in many organisms naturally and decomposes to water and oxygen. Its use avoids environmental problems associated with use of oxidizers. For applications where air availability is low or

nil, like high altitude applications or space and underwater applications, H_2O_2 is indeed the ideal choice among oxidizers.

Combining that with the use of aqueous solution of NaBH_4 as hydrogen carrying fuel brings significant added benefits. *Ease in controlled oxidation* the heat of hydrolysis of NaBH_4 is about 80 kJ/mole of H_2 as fuel, making it relatively easy to use the fuel in a low temperature polymer electrolyte fuel cell. *Simplified Membrane Electrode Assembly (MEA)* the catalytic electrodes and membrane electrolytes only need to be hydrophilic. Unlike ordinary H_2/O_2 fuel cells where both hydrophilic and hydrophobic phases are required to maintain a tenuous three phase interface at reaction sites use of liquid feed NaBH_4 and H_2O_2 considerably simplifies preparation of membrane electrode assemblies. *Lower polarization losses* Fast kinetics of the oxidation and reduction process and high mobility of the reactant/product ionic species significantly lowers the activation and mass transfer polarization losses and allows the fuel cell to operate at low temperatures

$\text{NaBH}_4/\text{H}_2\text{O}_2$ fuel cells offer significant operational benefits. *Compact and convenient all-liquid operation* the liquid-feed oxidant and fuel it is more than thousand times denser than gas phase reactants like air/oxygen and hydrogen. This large difference in mass densities has the potential to deliver significantly higher power/current densities. Traditional H_2/O_2 fuel cells are significantly hampered by the lack of efficient storage of H_2 and O_2 gases. *High specific energies* the liquid feed $\text{NaBH}_4/\text{H}_2\text{O}_2$ fuel cell can be operated at various pH of fuel/oxidant feed. As the pH varies the theoretical specific energies can change from 9.3 kWh/kg to 17 kWh/kg. Currently, the cost of fuel in a war-torn location is about US\$400 per gallon of gasoline. $\text{NaBH}_4/\text{H}_2\text{O}_2$ fuel cell will decrease the power costs significantly by packing high energy in devices with low weight and volume, clearly beyond the capacity of ordinary battery and fuel cell systems. These fuel cells will find use in future defense and space applications, like high power electric propulsion for surface rovers for Mars missions and potable high power sources for multifarious applications in warlike situations.

Design, Development and Characterization of the DBFC System

Studies are conducted with DBFCs employing Au as the cathode catalyst and Pt as the anode catalyst. It is possible to recycle the catholyte through the cell in DBFC comprising Au cathode catalyst unlike the one containing Pt cathode catalyst and hence utilization can be increased. These DBFCs are used in the self-supported DBFC system. In order to increase the energy density of the DBFC system, it is desired to reduce the weight of

anolyte and catholyte to as low a value as possible. To this end, concentrations of fuel and oxidant in the anolyte and catholyte, respectively, were kept high enough to store optimum amounts of the fuel and oxidant.

Optimization of oxidant concentration

Keeping the fuel concentration constant, the concentration of the oxidant is optimized. As received commercial 30 % H_2O_2 (~8 M) is used as the initial concentration for the optimization studies. Fuel concentration is kept as 8 wt. % NaBH_4 in 11 wt. % NaOH while oxidant concentration is varied between 8 M and 6 M H_2O_2 in 1.5 M H_2SO_4 . Figure 2 shows the polarization data for DBFC operated with 6 M and 8 M H_2O_2 while keeping the fuel concentration at 8 wt. % NaBH_4 in 11 wt. % NaOH . It is found that the performance for the DBFC with 6 M H_2O_2 is superior in relation to performance of the DBFC employing 8 M H_2O_2 . For galvanostatic operation of the DBFC, 50 ml of 8 M and 6 M H_2O_2 solutions are fed to the cell. Figure 3 shows the galvanostatic data for the cell employing 8 M H_2O_2 and 6 M H_2O_2 . From the data, it is seen that the operating time for the DBFC employing 8 M H_2O_2 is longer because of the availability of higher amount of H_2O_2 for the reaction. Accordingly, 8 M H_2O_2 in 1.5M H_2SO_4 is found to be optimum.

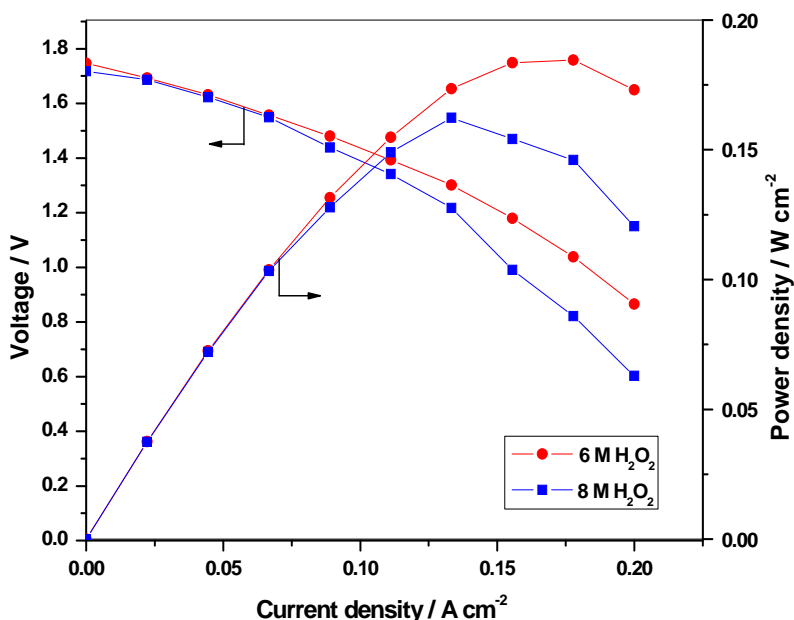


Figure 2. Polarization data for the DBFC with 6 M and 8 M H_2O_2 in aqueous 1.5 M H_2SO_4 as catholyte and 8 wt. % NaBH_4 in 11 wt. % NaOH as anolyte.

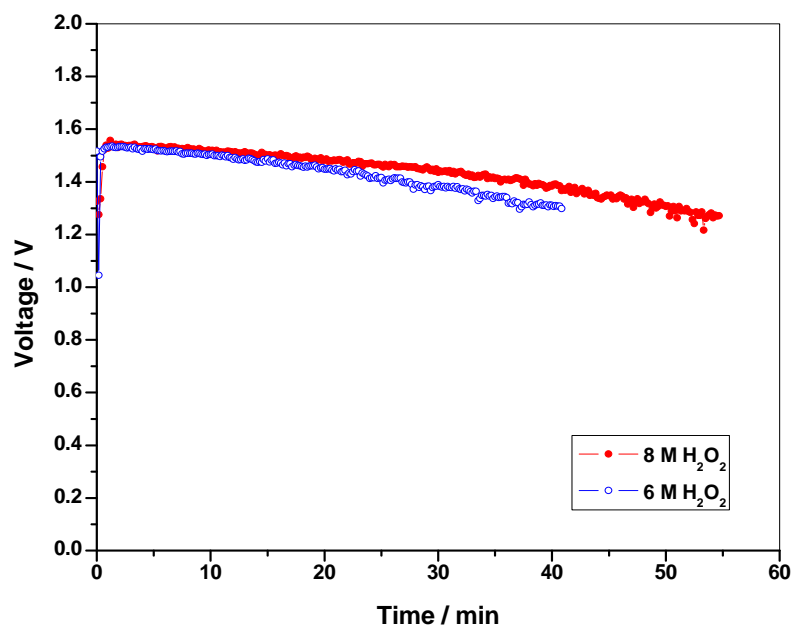


Figure 3. Performance data for the DBFC with 6 M and 8 M H_2O_2 in aqueous 1.5 M H_2SO_4 as catholyte and 8 wt. % NaBH_4 in 11 wt. % NaOH as anolyte at a load current-density of 65 mA cm^{-2} .

Optimization of fuel concentration

Since concentrations higher than 30 wt. % NaBH_4 in 11 wt. % NaOH is too viscous to be handled by a pump, optimization studies have been conducted using this concentration as the initial concentration. Keeping the oxidant concentration at 8 M H_2O_2 in 1.5 M H_2SO_4 , the peak power densities obtained (Figure 4) for 30 wt. %, 15 wt. %, 8 wt. % and 4 wt. % NaBH_4 in 11 wt. % NaOH are 50, 100, 160 and 200 mW cm^{-2} respectively. It is found that the performance for the DBFC with 4 wt. % NaBH_4 is superior to the performance for the DBFCs employing 30 wt. %, 15 wt. % and 8 wt. % NaBH_4 . For the galvanostatic study, 40 ml of 4 wt. % and 8 wt. % NaBH_4 solution with 50 ml of optimized concentration of 8 M H_2O_2 solution are fed to the cell and the data presented in Figure 5 show that solution containing 8 wt. % NaBH_4 sustains longer operating-time owing to the availability of higher amounts of NaBH_4 for the reaction. Accordingly, 8 wt. % NaBH_4 solution is considered to be the optimum. Based on these data, percentage values of fuel and oxidant utilized in the single cell are found to be 15% and 12.5%, respectively.

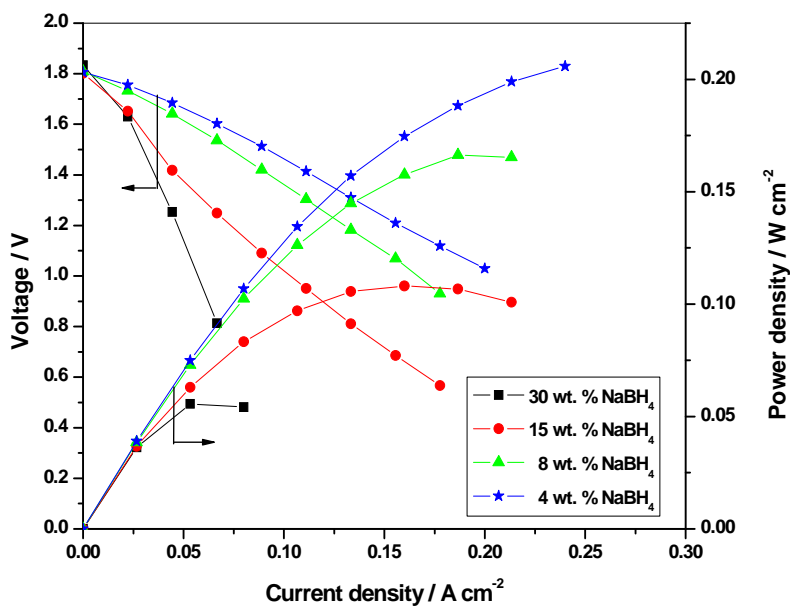


Figure 4. Polarization data for the DBFC with 4 wt. %, 8 wt. %, 15 wt. % and 30 wt. % NaBH_4 in 11 wt.% NaOH as anolyte and 8 M H_2O_2 as catholyte.

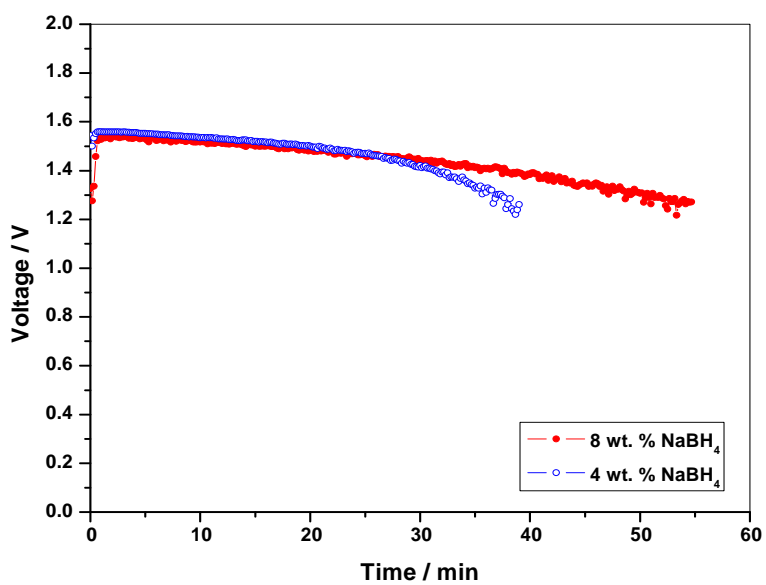
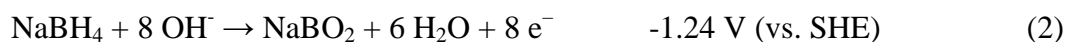


Figure 5. Performance data for the DBFC with anolyte containing 4 wt. % and 8 wt. % NaBH_4 and the catholyte containing 8 M H_2O_2 at a load current-density of 65 mA cm^{-2} .

Estimation of reaction products

In order to estimate the reaction products stoichiometrically we must know the reactions occurring at the anode and cathode.

At the anode of the DBFC, the following reactions can take place:



Sodium borohydride could concomitantly hydrolyse as:



Hydrogen thus generated may electrochemically oxidise at the anode as:



or it could be released to the atmosphere.

At the cathode of the DBFC, the following reactions can take place:

(a) Chemical decomposition of H_2O_2 occurs as follows:



Oxygen gas thus generated can be reduced to water as:



or it could be released to the atmosphere.

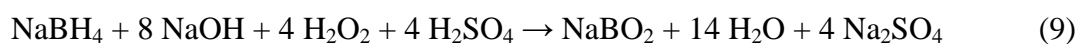
(b) Electrochemical reduction of H_2O_2 takes place as:



Na^+ ions pass through the membrane electrolyte and combine with the SO_4^{2-} ions to produce Na_2SO_4 as follows:



Accordingly, the net cell reaction can be written as:



The operating principle of the DBFC is depicted schematically in Figure 6.

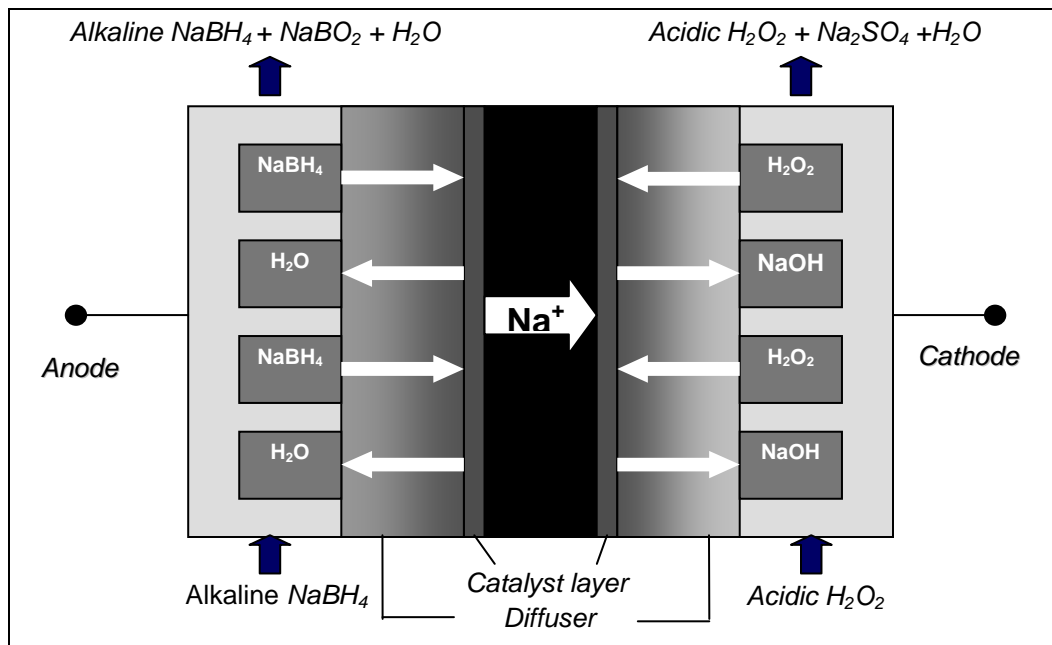


Figure 6. Operating principle of the DBFC.

As there are many possible sets of reactions that could take place concomitant with reactant crossover, it is hard to calculate the amount of reactants required using stoichiometric equations. Accordingly, studies were conducted to determine the amounts of fuel, oxidant and products in the initial and spent solutions. These studies were performed on a single cell using optimized concentration of anolyte and catholyte with an active area of 45 cm^2 and the results are summarized in Table 1.

Table 1. Stoichiometrically calculated and experimentally obtained values of reactants for given amount of fuel.

Reactant	NaBH ₄	NaOH	H ₂ O ₂	H ₂ SO ₄	Total
Stoichiometric (g)	x	8.46x	3.6x	10.37x	23.43 x
Experimental (g)	x	9.47x	4x	11.61x	26.08x + H ₂ O weight

The stoichiometric amounts of all the reactants are calculated according to reaction (9). For every gram of NaBH₄ electro-oxidized, 8.46 g of NaOH, 3.6 g of H₂O₂ and 10.37 g of H₂SO₄ are required stoichiometrically for the operation of the DBFC.

The amount of NaBH_4 electro-oxidized is determined by the charge (in coulombs) generated during the experiment. For example, if the total amount of NaBH_4 present in the anolyte is 1g and 30% of it is electro-oxidized and 50% hydrolyzed with 20% remaining unreacted, then the amount (x) of NaBH_4 that is electro-oxidized is equal to 0.3 g. The amount of NaOH consumed due to reaction and crossover from anolyte to catholyte is determined gravimetrically, albeit indirectly, by estimating the amount of SO_4^{2-} in the spent catholyte. From reaction (8), the amount of NaOH (in g) is estimated. Since some amount of NaOH crosses over from anolyte to catholyte, the quantity of NaOH required is always higher than its stoichiometric estimate. The amount of H_2O_2 is determined by permanganometry by titrating the initial and spent solutions against KMnO_4 . The amount $4x$ in Table 1 includes the amount (in g) of H_2O_2 electro-oxidized ($3.6x$) and decomposed ($0.4x$) into water and oxygen. The amount of H_2SO_4 consumed is determined by titrating the initial and spent catholytes against NaOH . From these data, it is seen that to generate a capacity of 5.67 Ah (1g equivalent of NaBH_4), a minimum of 25.08 g of H_2O_2 and supporting reactant need to be supplied to the system, excluding water.

Studies on the DBFC stack

Optimization of oxidant concentration

Keeping the fuel concentration constant at 8 wt. %, cell polarization data have been obtained for 8, 6, 4 and 2 M H_2O_2 in 1.5 M H_2SO_4 . For galvanostatic studies, 200 ml of 11wt.% NaOH solution containing 8 wt% NaBH_4 and 250 ml of 1.5 M H_2SO_4 solution containing 8 M H_2O_2 are fed to the stack. Unlike the single cell, the performance of the stack happens to be different while varying oxidant concentration as seen from the data in Table 2. The operation time increases as the concentration of H_2O_2 is decreased from 8 M to 2 M; this behavior can be attributed to rise in operating temperature of the stack as compared to the single cell. During the operation of the stack, H_2O_2 decomposition at cathode occurs as an exothermic (23.44 kcal/mole) reaction. It is noteworthy that an increase of 10 °C can enhance the decomposition rate of H_2O_2 by a factor of 2.3 which is typical of a first-order rate reaction. As the concentration of H_2O_2 in solution increases, less water becomes available to absorb the heat of decomposition. Above 2 M H_2O_2 , decomposition of H_2O_2 limits the operation time whereas the operation time for 1 M H_2O_2 is limited because it contains less amount of H_2O_2 than the amount required stoichiometrically while considering 14 % of fuel to be electro-oxidised. Accordingly, 2 M H_2O_2 is found to be optimum.

Table 2. Oxidant concentration optimization data for five-cell DBFC stack with 8 wt. % NaBH_4 and 11 wt. % NaOH .

H_2O_2 (M) in 1.5 M H_2SO_4	8	6	4	2	1
Operating time (min.)	37	41	47	52	36

Optimization of fuel concentration

Akin to single cell studies, the operating time for the DBFC stack using 4 wt. % NaBH_4 is less than DBFC stack using 8 wt. % NaBH_4 because of the availability of higher amounts of NaBH_4 for the reaction as seen from the data in Table 3. Accordingly, 8 wt. % NaBH_4 is taken to be optimum. In the present study, percentage of fuel and oxidant utilized by stack are found to be 14% and 47%, respectively.

Table 3. Fuel concentration optimization data for five-cell DBFC stack with optimized 8 M H_2O_2 in 1.5 M H_2SO_4 in aqueous media.

NaBH_4 (wt. %) in 11 wt. % NaOH	30	15	8	4
Operating time (min)	-	-	52	40

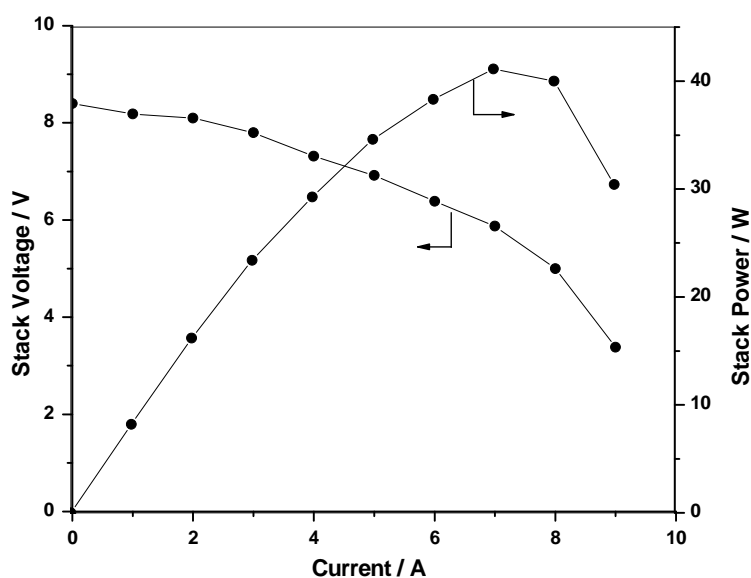


Figure 7. Polarization data for the DBFC stack.

Stack polarization

A maximum of 40 W is generated from this stack at a peak power-density of 180 mW cm⁻² at 5V as shown in Figure 7.

Self-supported DBFC system

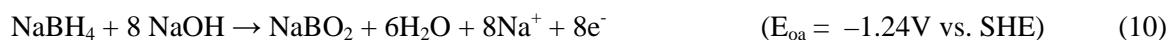
Among all the DBFCs studied, DBFCs employing Platinum as the anode and Au as the cathode catalyst are found to be advantageous in terms of power density and handling. A self-supported DBFC system is constructed based on DBFC employing these catalysts. Anolyte and catholyte containing optimized concentration of fuel and oxidant are fed to the DBFC stack of the self-supported system. The system sustains a net power output of 18 W with 2.1 W of auxiliary power consumption with an operational time of about 50 min.

Operating-time enhancement for the DBFC system

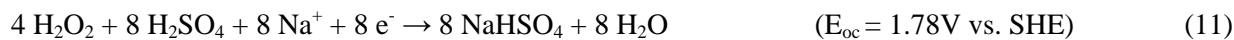
Since NaOH is consumed during the operation of fuel cell, operating time can be enhanced by increasing the concentration of aqueous NaOH. However, a maximum of 25 wt. % of NaOH can only be used, above which the solution viscosity becomes too high to operate the pump. This determines the maximum expected operating time to be ~ 113 min. It is noteworthy that increasing the aqueous NaOH concentration in the anolyte lowers the cathode performance.

Theory/Analysis

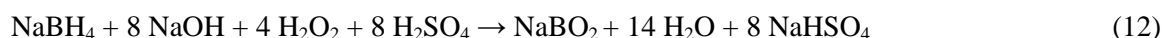
In developing the theoretical formalism for DBFCs we have used chemical reactions wherein, aqueous sodium borohydride, in presence of an alkali, is oxidized at the anode to sodium borate.



Sodium ions migrate through the Nafion membrane separator inside the fuel cell and take part in the cathode reaction.



The net cell reaction in such a DBFC is



Variations in the H₂O₂ reduction potentials with pH is governed by,

$$E(\text{H}_2\text{O}_2) = 1.78 - 0.059 \text{ pH} \quad (13)$$

Depending upon the pH of the H_2O_2 solution in the catholyte, the predicted value of cell potential varies between 1.64V – 3.02V, and the corresponding specific energy values change from 9.3 kWh/kg to 17 kWh/kg respectively.

However in practice output potential values are always significantly lower than the ideal/thermodynamic values and further decreases with increasing current density loads. These are due to activation losses, Ohmic losses and concentration losses. To minimize these polarization losses, fuel cell electrodes demand optimally designed electrode structures and catalyst morphologies. In this context, optimization modeling of DBFC is considered to be a valuable tool. This involves modeling mass transfer in fuel cells with a description of the movement of mobile species, material balances, current flow and fluid mechanics.

We consider a section of fuel cell consisting of two channels through which liquid feed catholyte and anolyte is passed. These reactants diffuse through the respective diffuser layers and reach catalyst layers where the reactions take place. The catalyst layers are separated by a modified Nafion membrane. The membrane facilitates the cell by allowing efficient transfer of Na^+ ions from anode to cathode and insulating electronic passage. Thus we have seven distinct regions for which modeling is done: 1) Anode diffuse layer 2) Anolyte channel 3) Anode catalyst layer 4) Membrane electrolyte layer 5) cathode catalyst layer 6) catholyte channel and 7) cathode diffuser layer.

Figure 8. The geometry of modeled section of fuel cell.

In these regions the model accounts for six distinct phenomenological processes: 1) conservation of electronic charge (using Ohm's law) 2) conservation of ionic charge (again via Ohm's law) 3) Butler-Volmer charge transfer kinetics 4) Flow distribution in gas channels (using Navier-Stokes' equation) 5) Flow in the porous diffuser electrodes (using Brinkman's equation) 6) conservation of mass in the liquid phase in both channels and porous electrodes (Diffusion and conduction).

Charge balance

The electronic charge balance in the anode and cathode current feeders is given by

$$0 = \nabla \cdot (-\kappa_s \nabla \Phi_s) \quad (5)$$

Here κ_s is the electronic conductivity and Φ_s is the electric potential in the solid electrode matrix. Similarly, the ionic charge balance valid in ionic conductor is

$$0 = \nabla \cdot (-\kappa_l \nabla \Phi_l) \quad (6)$$

Here κ_l is the ionic conductivity and Φ_l is the electric potential in the membrane region. In the anode and cathode catalyst layers, electrons are transferred between the ionic conducting electrolyte phase and the electronically conducting phase. This implies that the charge balance equations have current source terms present. The solid matrix phase will then have charge balance equation

$$-S_a i_{ct} = \nabla \cdot (-\kappa_s \nabla \Phi_s) \quad (7)$$

And the electrolyte phase will have equation

$$-S_a i_{ct} = \nabla \cdot (-\kappa_l \nabla \Phi_l) \quad (8)$$

where, $S_a i_{ct}$ denotes specific surface area times the charge transfer reaction current density. Note the current moving into electrolyte phase is taken as positive, which is the widely accepted sign convention followed in macrohomogeneous theory [2].

We assume Butler-Volmer charge transfer kinetics describe the charge transfer current density. At the anode, sodium borohydride is reduced and the following charge transfer kinetics equation thus applies:

$$i_{ct,a} = \frac{i_{0a}}{8F} \left\{ \exp \left[\frac{(1-\beta)8F\eta_s}{RT} \right] - \exp \left[-\frac{\beta 8F\eta_s}{RT} \right] \right\} \quad (9)$$

while for cathode the relationship is,

$$i_{ct,c} = \frac{i_{0c}}{2F} \left\{ \exp \left[\frac{(1-\beta)2F\eta_s}{RT} \right] - \exp \left[-\frac{\beta 2F\eta_s}{RT} \right] \right\} \quad (10)$$

where the notation used is standard.

For the ionic charge balance equations, we applied insulating boundary conditions at all external boundaries. At the interior boundaries, continuity in current and potential applies by default.

Mass transport

At the anode, a liquid-feed alkaline sodium borohydride is supplied as fuel. In the cathode, acidified hydrogen peroxide solution supplied. The material transport is described by the diffusion and convection equations

$$-D_{H_2O_2} \nabla^2 c_{H_2O_2} = R - \mathbf{u} \nabla c_{H_2O_2} \quad (11)$$

and

$$-D_{NaBH_4} \nabla^2 c_{NaBH_4} = R - \mathbf{u} \nabla c_{NaBH_4} \quad (12)$$

Equation 11 is applicable in the catholyte channel (with $R = 0$) and also in cathode catalyst layer (with $R = S_a i_{ct,c}/2F$). Similarly, equation 12 is applicable in the anolyte channel with ($R=0$) and also in anode catalyst layer (with $= -S_a i_{ct,a}/8F$). \mathbf{u} is the fluid velocity.

The boundary conditions at the walls of the channel and diffuser layers are zero mass flux (insulating condition). At the inlet, the composition is specified, while the outlet condition is convective flux. This assumption means that the convective term dominates the transport perpendicular to this boundary. Continuity in composition and flux apply for all mass balances at the interfaces between the catalyst layers and the channels.

Fluid flow

The weakly compressible Navier-Stokes equations govern the flow in the open channels:

$$\rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \left[-p \mathbf{I} + \mu \left\{ (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} (\nabla \cdot \mathbf{u}) \mathbf{I} \right\} \right]; \quad \nabla \cdot (\rho \mathbf{u}) = 0$$

Where p is pressure, μ is the dynamic viscosity, ρ is fluid density and superscript T indicates matrix transpose. In the porous catalyst layers, the Brinkman equations describe the flow velocity:

$$\left(\frac{\mu}{\xi} + Q\right) \mathbf{u} = \nabla \cdot \left[-p\mathbf{I} + \frac{\mu}{\epsilon} \left\{ (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} (\nabla \cdot \mathbf{u}) \mathbf{I} \right\} \right]; \nabla \cdot (\rho \mathbf{u}) = Q$$

where ϵ and ξ denote respectively, the porosity and permeability of the medium of the medium, and Q is the mass source term, which is related to the charge transfer current density.

The Brinkman Equation is integrated with the Navier-Stokes equation. All boundaries between porous and free subdomains are treated as internal boundaries.

At the inlet and outlet, the pressure was set, specifying a slight overpressure at the inlet to drive the flow (2 Pa at the anode, and 4 Pa at the cathode).

We chose the parameters such that they mimic experimental conditions [1].

Results and Discussion

A cross section of liquid feed direct borohydride fuel cell model was created and studied. The flow rates and temperatures were varied and the resulting changes in the polarization currents were analyzed. At higher flow rates there are higher pressure differentials in the flow channels resulting in higher mass transfer of the reactants. This results in higher power densities. We also varied the dimension of flow channels and found that the power densities again increases and reaches a maximum value before it drops. The current densities and power densities are found to be position dependent. With judicious flow channel optimization and diffusion layer thickness optimization we could reduce the fluctuations in the local current/power densities and obtain uniformity in the reaction kinetics in the catalyst layers. Furthermore the permeability and conductivity values were varied and the resulting effect on the performance of the fuel cell was studied. With increase in conductivities and permeability the power densities again increases. However the optimal flow channel designs depend upon conductivity and permeability values.

Summary/ Conclusions

A mathematical framework is developed for an all-liquid fuel cell. The fuel-cell uses alkaline solution of sodium borohydride as fuel and acidic solution of hydrogen peroxide as

oxidant. The fuel cell delivers about 30% higher voltage output, compared to H₂/O₂ fuel cells, under similar operating conditions, even though hydrogen constitutes about 11% in sodium borohydride. The fuel cell has the *highest energy density* per kilogram of fuel. The fuel crossover was found to be very small. This is attributed to the use of Nafion 117, which is about 175 µm thick. The Nafion 117 membrane was suitably modified for efficient transport of sodium ions from anode to cathode. The effect of pressure in flow channels on the performance levels of the fuel cell was analyzed. In general higher pressure increases the power densities. The effect of different operating conditions including concentrations of fuel/oxidant, temperature, pH, permeability and conductivity on the performance levels of the fuel cells were evaluated and conditions for optimal use of the power device was obtained.

Our studies also highlighted that due to the high energy densities, these all-liquid feed fuel cells are ideally suitable for integration in microscopic devices, including microchips with energy requirements in the milli-watt range. In these devices it will be critical to integrate existing and evolving engineering tools, such as microfluidics, MEMS, and NEMS, which offer another dimension of control at both the nano- and microscale. The creative use of microsystems and fluidic approaches make it possible to simultaneously control multiple operational parameters of fuel cells with a high level of precision over multiple operational needs in microdevices. At the same time there are significant challenges to be overcome. Among them is the need to understand and mitigate the precipitation of sodium borate in an operating fuel cell. All these problems will be looked into in the next phase of the study of DBFCs

References

1. R.K. Raman, N.A. Choudhury and A.K. Shukla, *Electrochemical and Solid-state Lett.* **7**, A488 (2004); N.A. Choudhury, R.K. Raman, S. Sampath and A.K. Shukla, *J. Power Sources* **143**, 1 (2005); R.K. Raman and A.K. Shukla, *J. of Applied Electrochemistry* **35**, 1157 (2005). P.S. Khadke, P. Sethuraman, P. Kandasamy, S. Parthasarathi and A.K. Shukla, *Energies* **2**, 190 (2009).
2. S F Sarner, *Propellant Chemistry*, Reinhold, New York, 1966.

Appendix

A. Personnel Supported:

- i) Professor A K Shukla, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India.

- ii) Professor S Sampath, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India.
- iii) Dr Alok K R Paul, Central Electrochemical Research Institute – Chennai Unit, CSIR Madras Complex, Taramani, Chennai, India
- iv) Dr. M K Ravikumar, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India.
- B. Publications: Manuscripts under preparation
- C. Interactions:
 - i) Professor K S Gandhi, Department of Chemical Engineering, Indian Institute of Science, Bangalore, India.
- D. Inventions:
- E. Honors/ Awards
- F. Archival Documentation:
- G. Software and/or Hardware